Changes in surface state density due to chlorine treatment in GaN Schottky ultraviolet photodetectors

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A chlorination surface treatment was used to reduce the surface density of states of a n-type GaN surface, which improves the Schottky performances of the resultant metal-semiconductor contact. Using capacitance-frequency measurement, the surface state density of the chlorine-treated GaN surface was about one order less than that without chlorination treatment. The dark current of the chlorine-treated GaN ultraviolet photodetectors (UV-PDs) is 1.5 orders of magnitude lower than that of those without chlorination treatment. The products of quantum efficiency and internal gain of the GaN Schottky UV-PDs without and with chlorination treatment under conditions of −10 V reverse bias voltage at a wavelength of 330 nm were 650% and 100%, respectively. The internal gain in chlorine-treated GaN UV-PDs can therefore be reduced due to a decrease in the surface state density. © 2008 American Institute of Physics. [DOI: 10.1063/1.2913344]

I. INTRODUCTION

Impressive progress has recently been made in III–V nitride-based compound semiconductors, which have been widely used in electronic devices and optoelectronic devices because of their inherent advantageous properties.1–4 For GaN-based electronic and optoelectronic devices, high-quality and reliable metal-semiconductor contacts are critical for gaining satisfactory performance. However, GaN-based compound semiconductors do contain high surface state densities. GaN Schottky ultraviolet photodetectors (UV-PDs) show a high internal gain as a result of hole trapping and electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density of III–V nitride semiconductors, which have been widely used in electronic devices and optoelectronic devices because of their inherent advantageous properties.1–4 For GaN-based electronic and optoelectronic devices, high-quality and reliable metal-semiconductor contacts are critical for gaining satisfactory performance. However, GaN-based compound semiconductors do contain high surface state densities. GaN Schottky ultraviolet photodetectors (UV-PDs) show a high internal gain as a result of hole trapping and electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6 The high inherent surface state density ultimately renders GaN semiconductors electron injection by surface states.5,6

II. EXPERIMENTAL PROCEDURE

The epitaxial structure of the GaN-based UV-PDs was grown using a metallorganic chemical-vapor deposition sys-

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FIG. 1. (Color online) Schematic configuration of GaN Schottky UV-PDs.

−term thermally stable ohmic metals were deposited on the n-type GaN surface of the UV-PDs using an electron-beam evaporator.12 Concentric ohmic contact rings (outer radius =260 μm, inner radius=210 μm) were patterned and then the samples were annealed in a N2 ambient at 700 °C for 1 min by a rapid thermal annealing system. The samples were divided into two groups and labeled as either samples A or B.
Prior to the deposition of the Ni/Au (2.5/2.5 nm) Schottky contact metals on the n-type GaN layer, the B samples were treated using chlorination surface treatment. The Schottky contact area of the B samples was connected with the Pt anodic electrode; the remaining area was protected by AZ-4620 photosensitive film. The Ni/Au (2.5/2.5 nm) metals used as a thin transparent conductive layer were first deposited. The Ni/Au (100/100 nm) pad with a diameter of 80 μm was then deposited on the center of the Ni/Au (2.5/2.5 nm) Schottky region using photolithography and the lift-off techniques.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The surface states of the GaN Schottky UV-PDs do not contribute to the capacitance at high frequencies since the associated charges cannot follow the high frequency signal. At high frequencies, the measured capacitance only consist of space-charge capacitance \( (C_{sc}) \), which can be expressed as

\[
C = C_{sc} \text{ (at high frequency)}. \tag{1}
\]

At low frequencies, the total capacitance is the sum of the space-charge capacitance \( (C_{sc}) \) and the interface capacitance \( (C_{ss}) \), which can be expressed as

\[
C = C_{sc} + C_{ss} \text{ (at low frequency)}. \tag{2}
\]

The surface state density \( (N_{ss}) \) can be expressed as

\[
N_{ss} = \frac{C_{sc}}{q^2 A}, \tag{3}
\]

where \( A \) and \( q \) are the area of Schottky region and the electron charge, respectively. The surface state energy \( E_{ss} \) below the conduction band \( (E_c) \) can be expressed as

\[
E_c - E_{ss} = q\Phi_b - qV, \tag{4}
\]

where \( q\Phi_b \) and \( V \) are the Schottky barrier height and the applied bias voltage, respectively. Figures 2(a) and 2(b) show the capacitance-frequency \( (C_f) \) curves measured at various forward voltages for the UV-PDs with and without chlorination surface treatment, respectively. At high frequencies, the similar capacitance values for chlorine-treated and untreated GaN Schottky UV-PDs were obtained. At a frequency of 100 Hz, the capacitance of chlorine-treated GaN Schottky UV-PDs is about one ninth of that for those without chlorination treatment at zero bias. According to our previous experimental results, the ideality factor \( n \) of 1.04 and 1.16 and Schottky barrier height \( q\Phi_b \) of 0.95 and 0.75 eV were obtained for the Ni/Au contact deposited on n-type GaN with and without chlorination treatment, respectively. Using Eqs. (1)–(4), the surface state density \( N_{ss} \) as a function of surface state energy \( E_{ss} \) can be determined and is hereby shown in Fig. 3. The surface state density \( N_{ss} \) of GaN Schottky UV-PDs without subjecting to chlorination treatment was varied from 1.9 \( \times 10^{12} \) eV\(^{-1}\) cm\(^{-2}\) \( (E_c - 0.75 \text{ eV}) \) to 4.4 \( \times 10^{12} \) eV\(^{-1}\) cm\(^{-2}\) \( (E_c - 0.45 \text{ eV}) \). On the other hand, the surface state density of chlorine-treated UV-PDs was varied from 2.1 \( \times 10^{11} \) eV\(^{-1}\) cm\(^{-2}\) \( (E_c - 0.95 \text{ eV}) \) to 3.5 \( \times 10^{11} \) eV\(^{-1}\) cm\(^{-2}\) \( (E_c - 0.65 \text{ eV}) \). The surface state density of the chlorine-treated GaN surface is about one order less than that of GaN without chlorination treatment. The chlorine-treated GaN Schottky UV-PDs can induce more Ga vacancies while causing the numbers of N vacancies to decrease due to the formation of GaCl\(_x\) and GaO\(_x\), respectively. Therefore, the lower surface state density of chlorine-treated UV-PDs can be attributed to the reduction in Ga dangling bonds and the passivation of nitrogen vacancies as a result of GaO\(_x\) formation.
The current-voltage ($I-V$) characteristics of the fabricated GaN UV-PDs were measured using an HP4145B semiconductor parameter analyzer. Figure 4 shows the dark current as a function of the reverse voltage of the GaN UV-PDs with and without the chlorination surface treatment. Nitrogen vacancy related surface states existed on the surface of $n$-type GaN generally result in a thin $n^+$ region on the surface. The $n^+$ region can allow electrons to tunnel through the Schottky barrier under reverse bias, thereby increasing the reverse leakage current. An increase in dark current with applied reverse voltage can also be attributed to the band bending, reduction in Schottky barrier height, and thermionic field emission. In chlorine-treated $n$-type GaN, the formation of GaOx decreases the surface states by reducing Ga dangling bonds and filling nitrogen vacancies. The dark current of chlorine-treated Schottky UV-PDs was 1.5 orders of magnitude smaller than that of those without chlorination treatment.

Figures 5(a) and 5(b) show the photoresponsivity as a function of wavelength for the GaN Schottky UV-PDs with and without the chlorination surface treatment, respectively. A xenon (Xe) lamp through a calibrated monochromator was used as the pumping source. The photoresponsivity of UV-PDs without chlorination treatment is larger than that of those being treated with such treatment. The photoresponsivity measured under conditions of $-10$ V reverse bias voltage and the wavelength of 330 nm of UV-PDs with and without chlorination treatment were 0.27 and 1.73 A/W, respectively. When a reverse voltage of $-5$ V was applied, the UV-visible rejection ratio of $10^4$ and $10^3$ was obtained for the GaN UV-PDs with and without chlorination treatment, respectively. The UV-visible rejection ratio of chlorine-treated GaN UV-PDs is about one order higher than that of those without chlorination treatment, which is ascribed to the reduction in surface states.

Figure 6 shows the product of quantum efficiency and internal gain as a function of reverse voltage at a wavelength of 330 nm of the resultant UV-PDs with and without chlorination surface treatment. The product of quantum efficiency and internal gain was measured using an HP4145B semiconductor parameter analyzer and a xenon (Xe) lamp through a calibrated monochromator as the pumping source in a dark box. The product of quantum efficiency and internal gain in the GaN Schottky UV-PDs can be calculated by the equation

$$ R = \eta G / \lambda $$

where $R$ is the photoresponsivity, $\eta$ is the quantum efficiency, $G$ is the internal gain, and $\lambda$ is the wavelength of the light.
chlorine-treated GaN Schottky UV-PDs can be effectively passivated, resulting in a smaller reduction in the Schottky barrier height and a smaller internal gain. 6,20 As shown in Fig. 6, the product of quantum efficiency and internal gain in chlorine-treated GaN Schottky UV-PDs slowly increased with increasing applied reverse voltage. An increase in the product of quantum efficiency and internal gain under optical illumination indicates an additional injection of electrons at a higher reverse voltage. 21 Because surface states at the metal-semiconductor interface could trap photogenerated holes, lowering the Schottky barrier height and producing additional gain in the UV photoresponse, 6, the smaller internal gain in the chlorine-treated GaN samples could be attributed to the effective reduction and passivation of surface states. The hole trapping effect, which is obvious at higher reverse voltages due to the narrow Schottky barrier width, causes more electrons to tunnel through the Schottky barrier. The product of quantum efficiency and internal gain of the GaN Schottky UV-PDs with and without chlorination treatment under a reverse voltage of −10 V at a wavelength of 330 nm are 100% and 650%, respectively.

IV. CONCLUSIONS

Chlorination surface treatment for n-type GaN reduces the surface states as a result of the decrease in Ga dangling bonds and the occupation of nitrogen vacancies caused by the passivation function of the GaO x formation on the chlorine-treated n-type GaN surface. Compared to the GaN Schottky UV-PDs without chlorination surface treatment, the chlorine-treated GaN Schottky UV-PDs show a lower dark current, a lower surface state density, a higher Schottky barrier, an ideal ideality factor, and a smaller internal gain. Internal gain in Schottky photodetectors is evidently induced by surface states; therefore, high performances of GaN Schottky UV-PDs could be expected if the surface states of the metal-semiconductor interface are significantly and effectively reduced.

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